GRAFT POLYMERIZATION. IV. FURTHER STUDIES OF THE INITIATION STEP IN THE GRAFT POLYMERIZATION OF VINYL MONOMERS ONTO CHROME-TANNED COLLAGEN*

M. M. TAYLOR, E. H. HARRIS, AND S. H. FEAIRHELLER

Eastern Regional Research Center†
Philadelphia, Pennsylvania 19118

ABSTRACT

In the process for the graft polymerization of vinyl monomers onto chrome-tanned collagen developed at the Eastern Regional Research Center, redox initiation with the persulfate-bisulfite combination is a key step. Various aspects of this reaction have now been examined and the results obtained permit improving the grafting and monomer conversion efficiencies. As monitored by iodometric titration, the partition of persulfate ion between water and collagen depends upon the persulfate ion concentration and the chrome content of the collagen. The rate of disappearance of persulfate ion from solution and the quantity absorbed increased with higher concentrations of persulfate ion or chrome content of the collagen. The implication is that both a mass action effect and ionic attraction are involved. Similar bisulfite ion distribution results were obtained in studies with a radioactive isotope of sulfur. In addition, monomer absorption was studied with the chrome-tanned collagen. All of these studies indicated that grafting takes place from monomer in the aqueous phase onto free radical sites generated on the collagen by the absorbed redox initiation system. Additional studies with different reducing agents used at varying molar ratios to the persulfate ion clearly indicated an optimum ratio which gave both maximum monomer to polymer conversion and grafting. The persulfate-bisulfite combination still appears to be the best.

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INTRODUCTION

The grafting of vinyl monomers onto chrome-tanned collagen has been investigated (1–5) as a means of achieving controlled permanent improvements in leather. The resulting leather has been found to be more uniform in thickness

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†Agricultural Research Service, U. S. Department of Agriculture.

and can be drycleaned without loss of polymer (5). The properties of the synthetic polymer can be combined with desirable qualities of natural leather. For example, the handle and/or stretch can be controlled by grafting a rubbery or nonrubbery polymer onto the leather.

Tanned and untanned collagen have been used as the substrate, with high energy radiation or redox systems as methods of initiation. From a practical standpoint the latter system, which is based on the ceric ion or persulfate ion, is probably the most satisfactory. The persulfate ion system was selected as being the more efficient and less expensive of the two. In addition, it did not impart a yellow color to the substrate or add additional heavy metal salts to the effluent as the ceric ion did in our experience. In our initial studies (1) the amount of unextractable polymer formed in the products was low, indicating limited grafting. While the amount of extractable polymer could be reduced by the use of polyfunctional co-monomers (5), it was believed that improvement should be sought through further study of the initiator system.

In these studies, the unextractable polymer has been referred to as grafted; however, it is recognized that there is little proof of such attachment. Recent studies (6) have shown that in the products formed with the persulfate ion-bisulfite ion redox couple, the portion of the polymer that is not extractable by ethyl acetate and acetone is covalently bonded to the protein. In order to understand more fully and thus control this complex reaction, we are engaged in a systematic study of the various parameters involved. The initiation part of the reaction is a multi-step reaction in which the redox couple first generates primary free radicals, which must then diffuse into the skin structure and generate secondary free radical sites on the collagen. It is at these collagen free radical sites that the grafted polymer is formed from monomer supplied by the emulsion.

In this study, the absorption of the reaction components by collagen was examined. The redox couple was studied separately as well as simultaneously and also during the actual graft polymerization. The persulfate ion partition was examined on chrome-tanned and untanned substrates. The possible effect that the presence or amount of Cr_2O_3 might have on the graft polymerization was examined over a wide range of chrome contents.

EXPERIMENTAL

Materials

Commercially chrome-tanned and pickled Nigerian sheepskins were obtained from various tanneries. The low inhibitor grade monomers and other chemicals and reagents were obtained from the usual commercial sources and were used as obtained.

Chrome Tanning and Analyses

Whole pickled Nigerian sheepskins were chrome tanned with various amounts

of a 33 percent basic chromium sulfate tanning agent according to the method of Fein *et al.* (7). Table I gives the grams of tanning agent per gram of drained pickled weight and the percent Cr_2O_3 obtained in each skin. Cr_2O_3 was determined by the official ALCA method (8).

TABLE I

Cr_2O_3 FIXED BY UNTREATED SKINS

Sample	G. Tan R per G. DPW*	%† Cr_2O_3
1	0.023	1.80
2	0.046	3.24
3	0.068	5.07
4	0.091	6.06
5	0.114	6.92
6	0.137	8.19

*Grams of Tan R offered per gram drained pickled weight (DPW).

†Cr_2O_3 content of skin based on moisture-free basis.

Depickling Procedure

The Nigerian sheepskins were depickled by tumbling them for two hours in a 200 percent float containing ten percent sodium acetate and ten percent sodium chloride, all based on the drained pickled weight, and then washed thoroughly in running tap water.

Persulfate Partition Study

Depickled or chrome stock was cut into pieces so that sufficient material, containing 4.45 grams of dry substance, could be added to each flask. Potassium persulfate was made up to a known concentration and appropriate aliquots were added to each flask. These aliquots were chosen to give four, eight or 16 percent of the dry substance as potassium persulfate. Additional water was added as necessary to give a 200 percent float based on the drained skin weight. The total water content of each flask (*i.e.,* water in skin plus water added) was 70.5 ml. The flasks were stoppered and shaken for 10, 20, 30, 60, 120, 240, and 360 minutes. A separate sample was used for each time interval.

At the appropriate time, a 25 ml. aliquot was taken and the residual persulfate concentration was determined by a slightly modified iodometric titration (9). The modification involved the use of a two hour (rather than the prescribed 30 minute) reaction time for the oxidation of the iodide by the persulfate. The percent persulfate lost from solution was calculated from these data.

Bisulfite Partition Procedure

Pieces of chrome-tanned Nigerian sheepskin (5.28 grams of dry substance) were placed in 125 ml. Erlenmeyer flasks. The drained blue weight (DBW) was 25.0 grams, and a 200 percent float was added to each flask. Eight different samples were run in duplicate, and $K_2S_2O_8$ and/or $NaH^{35}SO_3$‡ were added as indicated in Table II. The $NaH^{35}SO_3$ (5.23×10^4 counts per minutes (c.p.m.)/mg.) was made up into a solution, and aliquots of this were added to each float

TABLE II

^{35}S-TAGGED $NaHSO_3$ PARTITION STUDY

Run	%* $NaHSO_3$	%* $K_2S_2O_8$	Moles $NaHSO_3$ to 1 Mole $K_2S_2O_8$	% $NaH^{35}SO_3$ Removed from Float (minutes) 10	20	30	60	120
1	1.33	0	—	53	62	76	87	92
2	1.33	1.33	2.60	58	66	75	85	90
3	1.33	2.67	1.30	52	68	74	81	88
4	1.33	4.00	0.86	50	60	72	80	85
5	4.00	4.00	2.60	47	54	65	74	76
6†	1.33	4.00	0.86	40	56	68	80	82
7	0.28	4.00	0.18	44	59	60	73	82
8	0.55	4.00	0.36	54	64	68	76	82

*Percentages based on skin's dry substance.

†Graft polymerization run with 33.3 percent methyl methacrylate based on skin's dry substance and Triton X-100 as emulsifier.

to yield a known concentration at time zero. The flasks were stoppered and shaken for the appropriate time period. Duplicate ten μl. aliquots were taken at 10, 20, 30, 60, and 120 minutes. Removal of aliquots of this size would have a negligible effect on the concentration of the reactants in the remaining solution. Each aliquot was placed in a scintillation vial, scintillation cocktail was added, and the concentration of ^{35}S-containing ions was then determined by measuring the radioactivity in each sample with a Nuclear Chicago Mark II** Scintillation Counter. From the above data the percent ^{35}S-containing ions lost from solution was calculated in terms of $NaHSO_3$.

Effect of the Molar Ratio of Reductant to Oxidant in the Redox System

Pieces of chrome-tanned Nigerian sheepskin (50–70 grams as DBW) were placed in one quart Mason jars, and graft polymerized with methyl methacryl-

‡To avoid the release of SO_2, do not contact sodium bisulfite with acids. In this case the danger is compounded by the use of a radioactive isotope of sulfur.

**Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

ate†† equal to 33.3 percent of the dry substance as in our previous publication (1) with one of the reducing systems listed in Table III. Duplicate runs were made in all cases. The samples were then washed in running tap water, air dried, and finally prepared for analyses as described in an earlier publication (1).

Free Radical Partition Study

A Mason jar, pieces of chrome-tanned Nigerian sheepskin, solutions of $K_2S_2O_8$, solutions of $NaHSO_3$ and a solution of Triton X-100 were placed in a glove bag. This was evacuated (*ca.* 78 Torr) and then refilled with nitrogen (*ca.* 760 Torr). Four cycles were used to reduce the oxygen content to a noninterfering level. All components were combined in the jar, which was then sealed, removed, and tumbled for 30 minutes. The glove bag was used, as before, to permit transfer of the initiated skin to a new jar containing the same amount of water and emulsifier but no further source of redox initiator. Methyl methacrylate, equal to 33.3 percent of the average dry substance of the skin, was added to the jar containing the transferred, initiated skin, water, and emulsifier. This same amount of monomer was also added to the jar containing the original initiating system. This partition scheme is illustrated in Figure 1.

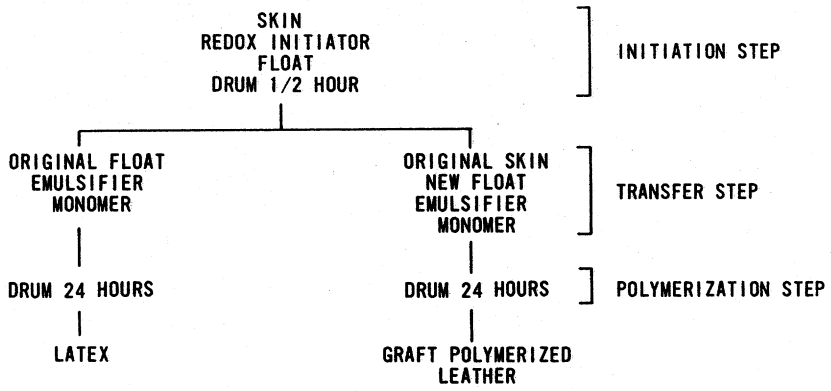


FIGURE 1.—Flow diagram for free radical partition study.

This experiment was carried out in duplicate for the reductant/oxidant molar ratios of 0.85/1.0 and 0.18/1.0. Tumbling was continued for 24 hours. The grafted leather was then handled as before and analyzed. The jars containing the original initiator solution plus monomer formed a typical latex and had a slight monomer odor.

Graft Polymerization on Stock Containing Various Amounts of Cr_2O_3

The chrome stock, tanned as in Table I, was graft polymerized with methyl

††Appropriate care must be taken in handling all monomers owing to the possible flammability and the toxic nature of these chemicals.

methacrylate after initiation with four percent $K_2S_2O_8$ and 1.33 percent $NaHSO_3$ (based on the dry substance), as previously described. This graft polymerization was similarly carried out using 30.6 percent methyl methacrylate plus 2.66 percent methacrylic acid (based on the dry substance). Analyses were made as described.

Monomer Partition

Pieces of chrome-tanned sheepskin (50–70 grams) were placed in one quart Mason jars whose lids were equipped with a septum. Graft polymerization was carried out in the usual manner with *n*-butyl acrylate equal to 33.3 percent of the dry substance of the chrome stock. A similar run was made without the initiator system. Approximately 0.2 ml. aliquots were periodically removed, and 1 μl. of each was injected into a Varian model 1520B Gas Chromatograph. The rate of disappearance of monomer from the aqueous phase was measured. At the end of each run, the skins were analyzed as previously described.

RESULTS AND DISCUSSION

Persulfate Ion Partition

Earlier studies have shown the effectiveness of the persulfate ion as the oxidant in the redox system (1–5). As a first step in developing a better understanding of the redox initiation system, the persulfate ion partition was examined with both tanned and untanned collagen. We did not attempt to determine the maximum take-up of the persulfate ion by the collagen for the following reasons. If this were a weak surface binding, the value would obviously be large and probably even larger than if ionic binding were the only mechanism. Since collagen has some 83 to 95 equivalents of basic side chains per 10^5 grams (10), this could bind as much as approximately 26 percent of the dry weight of the collagen when using $K_2S_2O_8$. In all these ion partition studies, there would be no reason for the ions to leave the polar environment of water unless to go to a more cationic environment. Collagen supplies this, and it becomes increasingly cationic with the higher chrome contents. Therefore, the rate of partition was examined when using amounts of $K_2S_2O_8$ closer to those employed during an actual graft polymerization run and for time periods appropriate to the earlier phase of the reaction.

Commercially tanned Nigerian sheepskin was used, with the amount of $K_2S_2O_8$ offered based on four, eight, and 16 percent of the dry substance. The rate of disappearance was measured for two hours (Figure 2). The curves show the grams of potassium persulfate lost from solution, in the presence of chrome-tanned skin, over the two hour period. Each curve obtained has a corresponding horizontal line to indicate the limit in grams of persulfate that could have disappeared at that particular level. In addition, a pip indicates the calculated point where the loss of persulfate from solution would correspond to a mere equilibra-

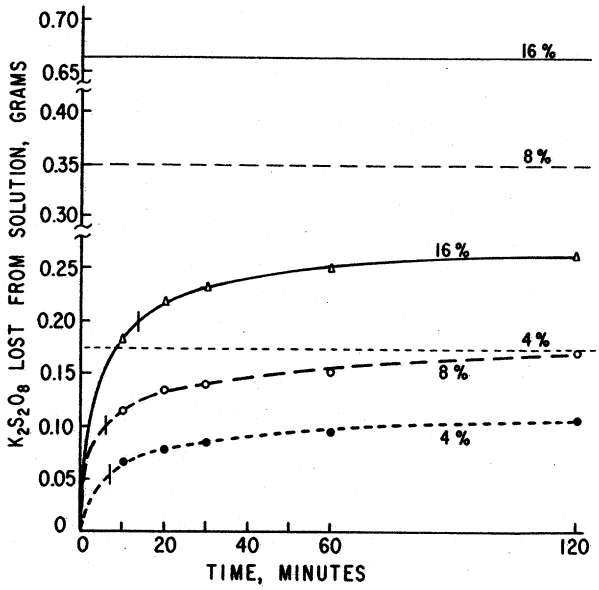


FIGURE 2.—Partition study using four, eight, and 16 percent $K_2S_2O_8$.

tion of the persulfate added in solution with the water contained in the skin itself. This point was reached in the first six to thirteen minutes under the existing conditions of this experiment. None of the levels studied was exhausted at the end of the two hour period. When the recommended four percent level was used, 48 percent of the $K_2S_2O_8$ offered was lost after 30 minutes (the customary period prior to addition of monomer). Under redox initiation conditions this value could not be applicable. Loss from solution implies absorption by the skin but does not explain the fate of the persulfate. Early studies showed that, at room temperature, persulfate ion alone could not initiate polymerization on chrome-tanned stock (1). This would indicate a lack of chemical reaction within the skin in terms of a redox mechanism. Reaction with the chrome content of the skin might also be possible. Evidence, presented later, suggests that, if this does occur, it is in a nondestructive manner in terms of tannage or the further availability of the persulfate ion itself.

The apparent mass action effect seen in Figure 2 suggests that, as far as the persulfate ion is concerned, the initiation step might be shortened if the persulfate ion were offered in a more concentrated float than is presently used. This float could then be lengthened as needed at the time of monomer addition.

The next phase of the investigation was on the possible effect that chrome tanning might have on the persulfate ion absorption. For this study, the four percent level of the $K_2S_2O_8$ (the amount normally employed in the reaction) was used. Three levels of chrome were used, with depickled Nigerian stock

representing the zero chrome level (Figure 3). The commercially chrome-tanned stock was from a different tannery than that referred to in Figure 2. The results show a trend for a faster and more complete absorption of persulfate ion in the presence of chrome-tanned stock than in the depickled stock, at least during the 6½ hour period of this study.

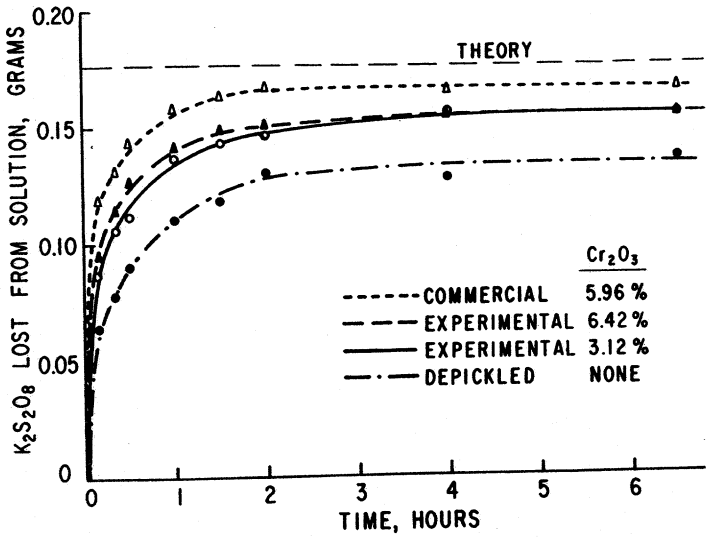


FIGURE 3.—Effect of skin's chrome content on partition of four percent $K_2S_2O_8$.

The depickled stock was at about the same pH as the chrome-tanned stocks and gave no particular problems in "plumping." Although this depickled stock absorbed at a slower rate than the various chrome stocks, it still removed about half of the available persulfate in the first 30 minutes and about three quarters in 6½ hours. The two experimentally tanned chrome stocks gave almost identical rates. This curve is intermediate to those of the depickled and the commercially tanned stocks. While there is no simple and complete explanation for the greater persulfate uptake by the commercially tanned stock, it might be related to that particular tanning process, including the presence of masking agents. In general, these results suggest that the persulfate ion could be bound by the chrome complexes in addition to ionic sites supplied by collagen itself.

The data show that collagen, with or without chrome-tanning, absorbs persulfate ions from solution, but there is a question of the future availability of the ions in the redox initiation system. The lack of change in the shrink temperature of chrome stock after persulfate ion absorption indicates that any involvement with the chrome complex is not destructive.

To determine if the lost persulfate ion was present within the skin and could

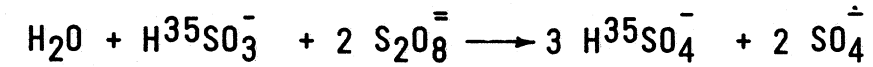
still participate in redox initiation after absorption, the following experiment was carried out. The usual float was used, and potassium persulfate (four percent of the skin's dry weight) was added along with the chrome stock. This was shaken for one hour at room temperature. Iodometric analysis of the float showed that 88 percent of the available persulfate was lost from solution. The skin was then placed in a fresh float of only water and again shaken for one hour. At this point a second fresh float was used for another hour. Iodometric analysis of each of these floats showed that the skin presumably still held 86 percent of the offered persulfate ion.

This skin was then added to a float containing emulsifier and sodium bisulfite but no additional persulfate. The jar was purged and then tumbled for 30 minutes before methyl methacrylate (equal to 33 percent of the skin's dry weight) was added. The jar was again purged and tumbled 24 hours.

The skin was washed, dried, and analyzed. The total polymer amounted to 22.8 percent and the bound polymer was 12.8 percent. The theoretical total polymer value is approximately 24.8 percent. These results show that absorbed persulfate ion is not readily desorbed by water, does not lower the chrome stock shrink temperature, and is available for graft polymerization at least for three hours after absorption.

Sodium Bisulfite Partition Studies

The studies with sodium bisulfite were monitored by incorporating ^{35}S as a tracer, since iodometric analysis could not be used in the presence of persulfate ion. The tagged ions are not the free radical ions; only the bisulfite ions or their oxidation product, the bisulfate ions, are (Figure 4). The stoichiometric ratio of mole of reductant per mole of oxidant is 0.5. This ratio is referred to later.



THEORETICAL MOLAR RATIO OF REDUCTANT TO OXIDANT IS 0.5 TO 1.0

FIGURE 4.—Equation for redox reaction.

Chrome-tanned Nigerian sheepskin was used in this series of experiments with the usual 200 percent float based on the drained weight. The amount of sodium bisulfite used was varied as in Table II. Periodic removal of small aliquots permitted the measurement of the rate of disappearance of the tagged ions from the float, but could not discriminate beween the tagged bisulfite and the resulting tagged bisulfate ions formed when potassium persulfate was present.

The partition was monitored when sodium bisulfite was used alone, in a redox system (at various molar ratios), and also during an actual graft polymerization. The data from Runs 1, 4, and 6 of Table II yield a family of curves showing the observed rates of disappearance of the tagged ions under these conditions (Figure 5). The general shape of the curve for loss of bisulfite alone from solution is similar to that previously seen for persulfate ion. The rate of disappearance of bisulfite from solution is higher when it is present by itself than when persul-

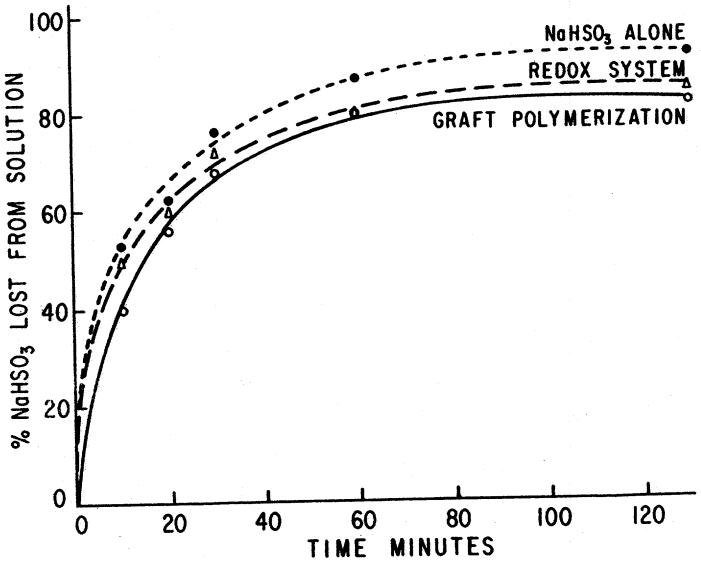


FIGURE 5.—Partition with $NaHSO_3$ under different reaction conditions.

fate ion is present, and its rate of disappearance during an actual graft polymerization is even lower. These rates probably reflect the competition resulting from the larger number of ions present in the redox system and from the presence of the monomer and emulsifier during the graft polymerization. As seen later, the molar ratio of reductant to oxidant can have a profound effect on the total and bound polymer contents. Runs 7 and 8 were made with two of the molar ratios that were more efficient than the previously recommended value used in Run 4. Although the concentration of bisulfite ion was lower in Runs 7 and 8 than in Run 4, only small differences were seen in the rate of disappearance of the tagged ion for these runs.

Various Reductants and Molar Ratio Studies

In earlier investigations at this laboratory (1), the emulsifiers were varied as well as the atmosphere, the levels of oxidant, and the period of initiation. A

comparison of various reductants used at a single level showed sodium bisulfite to be the most practical choice (3). Some more comprehensive studies on this part of the initiation reaction can now be reported.

Potassium persulfate was kept at four percent of the skin's dry weight. The amount of each reductant was then compared in terms of its molar ratio to the oxidant. Although 0.5 mole of reductant to one of oxidant is the theoretical ratio (Figure 4), at least one other investigator has found an even lower ratio to be effective in conventional emulsion polymerizations (11). By the use of a series of these molar ratios of reductant to oxidant, a logical comparison could be made between different reductants to determine the best molar ratio for any given reductant. All runs were made in duplicate and analyzed in the usual manner.

Figure 6 shows the results obtained with potassium persulfate and sodium bisulfite. The molar ratio is plotted on the abscissa and the polymer content is

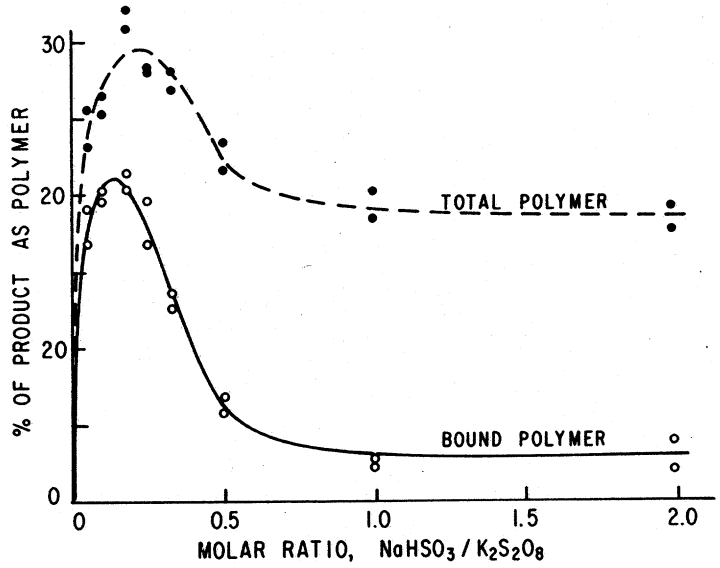


FIGURE 6.—Polymer analysis found with varying molar ratios of redox couple $NaHSO_3/K_2S_2O_8$.

on the ordinate. The upper curve represents the total polymer content of the product, and the lower curve the bound polymer, also on a product basis. The similarity of shape of these curves and those in Figures 7 and 8 is interesting in itself, but even more so is the fact that all the reductant studies listed in Table III are of the same shape, although of somewhat different numerical values.

The general comments that can be made about Figure 6 can be applied to all the systems listed in Table III. Thus, the lowest yields of either total or bound polymer were found when the molar ratio of reductant to oxidant was

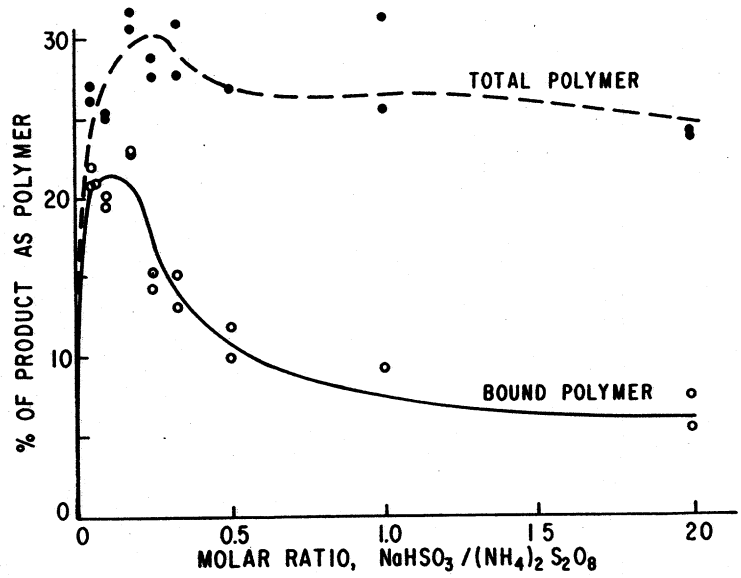


FIGURE 7.—Polymer analysis found with varying molar ratios of redox couple $NaHSO_3/(NH_4)_2S_2O_8$.

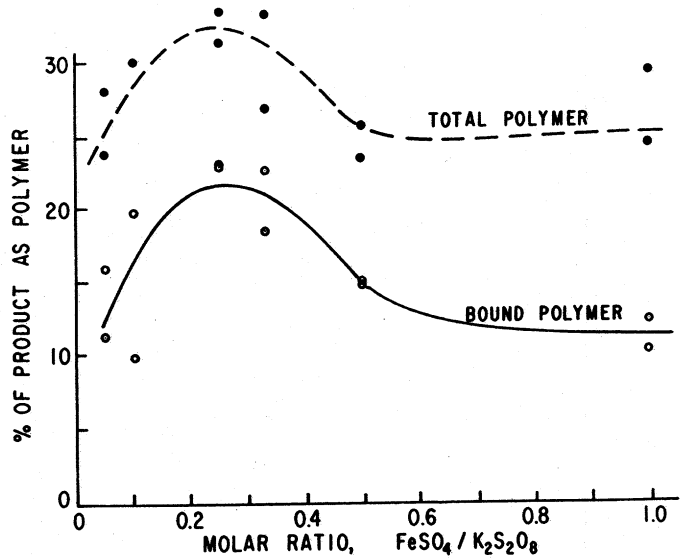


FIGURE 8.—Polymer analysis found with varying molar ratios of redox couple $NaHSO_3/FeSO_4$.

TABLE III

REDUCING SYSTEMS AND MOLAR RATIOS STUDIED

Reducing Systems	Moles of Reducing Agent/Mole $K_2S_2O_8$*								
	.05	.10	.18	.25	.33	.50	.85	1.00	2.00
$NaHSO_3$	X	X	X	X	X	X	X	X	X
Tetrakis†	X	X		X	X	X		X	X
Tetrakis/$NaHSO_3$‡	X	X		X	X	X		X	X
$CH_2OHOSONa$	X	X	X	X	X	X		X	X
$FeSO_4$	X	X		X	X	X		X	X
$FeSO_4/NaHSO_3$‡	X	X		X	X	X		X	X

*$(NH_4)_2S_2O_8$ was also used at these molar ratios, but only with $NaHSO_3$.

†Tetrakis hydroxymethyl phosphonium chloride.

‡Each component of reductant pair supplied 50 percent of moles needed for each ratio studied.

varied from 2.0 through the stoichiometric value of 0.5. It was only at the highest ratio that occasional homopolymer was ever found external to the treated stock. As the molar ratio was further lowered from 0.5 to 0.18, both the total and bound polymer curves rose to their maximum values. Further reduction in the molar ratio from 0.18 to 0.05 caused the curves to reflect lessening amounts of polymer, but still well in excess of those obtained with the range of molar ratios from 0.5 to 2.0. As the molar ratios were lowered from 2.0 to 0.18, the percentage of the total polymer that was bound increased to its maximum and then declined somewhat over the range of molar ratios 0.18 to 0.05. The maximum polymer yields and grafting efficiency seen at the 0.18 molar ratio and the other common factors found in the curves obtained with the various reductant systems listed show the probable presence of a uniform reaction mechanism. This mechanism is not yet fully understood. It is probably related to a compromise of having sufficient primary free radicals to initiate the secondary free radical.

Since the persulfate level is fixed at four percent of the skin's dry substance and the reductant level is varied, the maximum quantity of free radicals would require at least the stoichiometric amount of reductant. This was found for the molar ratios of 0.5 through 2.0. It is over this range that the lowest polymer yields were found. These low yields could have been caused by the high concentration of free radicals and the increased probability of their mutual termination before diffusing into and initiating the skin. As the amounts of reductant were further reduced to less than the stoichiometric ratio, the quantity of free radicals that could be found was lowered. This reduced the chance for mutual termination of the primary radicals and hence increased the probability of forming the necessary collagen free radicals. Continued reduction below the 0.18 molar ratio that produced the maximum monomer to polymer conversion and grafting effici-

ency, then produced an even lower quantity of free radicals and a consequent reduction of grafting sites. Since fewer sites were available, the amount of polymer of any type that could form had to be reduced and indeed this did happen over the range of 0.18 to 0.05 molar ratios.

Figures 7 and 8 illustrate the similarity of shape of the curves as well as the differences found in the numerical values. A prime consideration in all these studies was to understand the reactions as fully as possible in order to develop a practical and completely reliable graft polymerization process. The reductant system used in Figure 8 is not presently considered practical because of a mottled stain over the grafted product from the iron salt but is included to demonstrate the uniform finding that the 0.18 molar ratio produced the best total and bound polymer contents.

Figure 7 demonstrates that the ammonium form is as effective as the potassium persulfate when used in an equivalent amount and with the same reductant. It also shows the variation in amount of polymer formed which seems to be related to the choice of reductant itself. For example, the total polymer content in the grafted leather obtained over the molar ratios 2.0 to 0.5 was definitely higher with the use of ammonium persulfate instead of the potassium salt. The bound polymer content of the grafted leather also was higher with the use of the ammonium salt, which, as a practical matter, is less expensive.

Identification of the Method of Graft Formation

The possibility exists that the grafted polymer is formed by having large molecular weight polymer radicals form in the emulsion and then terminate onto the collagen. Two experiments were designed to test this possibility.

The skin was initiated, then separated from that float, and transferred to a new float containing only monomer and emulsifier (Figure 1). This transfer was done under an inert atmosphere in a glove bag, which avoided any interference in the reaction from atmospheric oxygen. Two different molar ratios of reductant to oxidant were used and the results were compared to those of similar runs carried out without the transfer step (Table IV). The numerical differences were within experimental error and show that after 30 minutes sufficient free radicals were present within the skin to initiate graft polymerization, whether the transfer step was used or not. At the ½ hour point, sufficient free radicals were still present in the original float to form a latex. From a mechanistic standpoint, these results suggest that the grafted polymer is more likely formed from sites on the collagen rather than from high molecular weight polymer free radicals that terminate onto the collagen. However, these results do not answer the question of why, during a normal graft polymerization reaction, no polymer forms in the float. One explanation is that, if it does, the latex so formed is absorbed into the leather and is present as an extractable homopolymer.

Chrome-Graft Polymerization Study

The amount of persulfate ion absorbed by collagen increased with the presence of chrome tannage. The following series of experiments was designed to determine if the amount of chrome present might affect the graft polymerization reaction. Pickled Nigerian stock was tanned with increasing amounts of Tanolin

TABLE IV

EFFECT OF FREE RADICAL PARTITION ON POLYMER ANALYSIS

$HSO_3^-/S_2O_8^=$** Molar Ratio	Percent Polymer*	
	Total	Bound
	Transferred	
0.85/1.0	29.6	9.0
0.18/1.0	26.4	21.0
	Nontransferred	
0.85/1.0	25.0	7.2
0.18/1.0	32.2	21.4

*Percent polymer is a weight percent calculated on a moisture-free and ash-free basis. Total polymer is calculated from the nitrogen analyses of control and treated pieces. Bound polymer is obtained by correcting the total polymer for the amount extracted by ethyl acetate.

**$K_2S_2O_8$ was added based on four percent of dry substance. The amount of $NaHSO_3$ added was calculated by using the appropriate molar ratio.

TABLE V

EFFECT OF CHROME CONTENT ON POLYMER CONTENT OF GRAFTED LEATHER

Cr_2O_3 in Leather (%)**	MMA* Percent Polymer‡		MMA/MAA† Percent Polymer‡	
	Total	Bound	Total	Bound
1.80	26.6	15.4	25.6	22.9
3.24	27.0	12.1	26.4	23.2
5.07	28.0	14.1	26.2	24.0
6.06	26.8	11.8	26.9	23.1
6.92	26.0	12.0	25.6	22.8
8.19	28.2	12.9	26.7	23.8

*Methyl methacrylate (MMA), 33.3 percent of the dry substance.

†Methyl methacrylate, 30.6 percent of dry substance plus methacrylic acid (MMA), 2.7 percent dry substance.

‡Percent polymer is a weight percent calculated on a moisture-free and ash-free basis. Total polymer is calculated from the nitrogen analyses of control and treated pieces. Bound polymer is obtained by correcting the total polymer for the amount extracted by ethyl acetate.

**Cr_2O_3 content of skin based on moisture-free basis.

R. This stock was then graft polymerized with methyl methacrylate in one series and the combination methyl methacrylate/methacrylic acid in the other series, with these monomer(s) offered as 33.3 percent of the dry substance (Table V). The uniformity of the total polymer content reflects the essentially theoretical yield obtained, regardless of chrome content, and indicates that the amount of chrome present has no apparent effect on the grafting reaction. Thus the level of chrome present in the leather is more properly dependent on the tanneries' requirements for a particular end use. The total polymer data are in slightly higher values than the theoretical value of 25 percent. This is due partly to the nonuniform nature and water content of the drained blue stock and partly to limitations imposed by the analytical method itself.

Monomer Partition Study

Monomer could be removed from the float by either a fatliquor type mechanism or an actual polymerization, or both. A gas liquid chromatography technique was used to follow the monomer concentration in the float, with and without the redox system being used. The resulting data are illustrated in Figure 9.

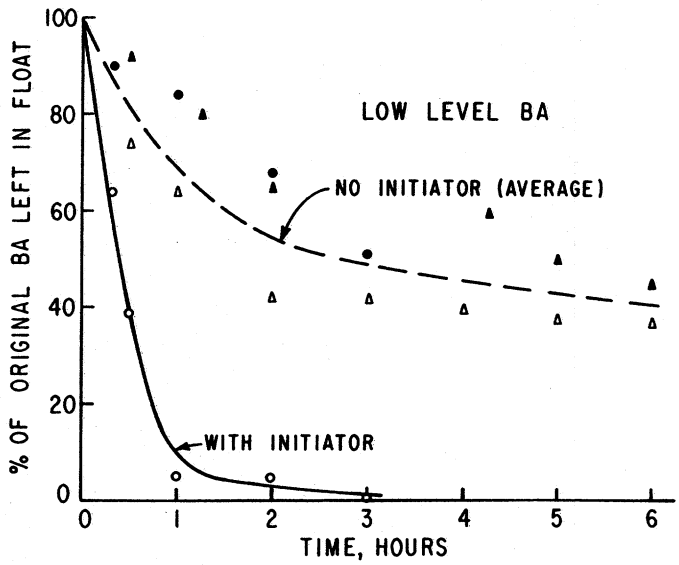


FIGURE 9.—*n*-Butyl acrylate partition study with and without redox initiation. BA = *n*-butyl acrylate.

The relative lack of stability of the emulsion as it formed under the mild agitation used caused some variation in the results obtained without the redox system present. This was due to partial breaking of the emulsion during the period between sampling and injecting into the chromatograph. Three such runs were

made and the results plotted to show the common trend, represented by the broken line, indicating that about 60 percent of the monomer offered has been taken up by the skin. The loss of monomer under these conditions is caused by a fatliquoring type mechanism and demonstrates that the emulsion can supply sufficient monomer for the grafting reaction itself that occurs at the initiated sites on the collagen.

Analyses of the product showed 2.9 percent as total polymer and 1.8 percent as bound polymer. With the initiator system present, a much more rapid rate of monomer disappearance was seen. At the end of one hour 95 percent of the monomer was removed from the float, and at the end of three hours only a trace was detectable. This graft-polymerized product contained 28.7 percent as total polymer and 15.7 percent as bound poylmer. These results, combined with those of the free radical partition study, seem to imply rather strongly that the graft is formed by a collagen free radical as the site of graft polymerization and that the emulsion merely supplies the monomer to build the chain.

SUMMARY

Results of the persulfate ion partition with collagen show that the rate is increased by both a mass action effect and the presence of chrome in the form of the crosslinks formed during tanning, and that the persulfate ion does not adversely affect the shrink temperature of the tanned stock and is not readily re-extracted by water, yet, in this bound form, is available for at least three hours as the redox oxidant.

The data obtained in this study also show that, regardless of the reductant system used, the bound polymer and, more importantly, the grafted polymer contents were greatest with the use of a 0.18 molar ratio of reductant to oxidant. The most efficient redox couple was $(NH_4)_2S_2O_8$ and $NaHSO_3$.

As to the grafting reaction itself, the most probable mechanism entails formation of a collagen free radical that combines with monomer from the emulsion to yield the grafted chain.

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DISCUSSION

DR. WILLIAM PRENTISS (Rohm and Haas Company): Any study which clarifies a chemical process is of very great importance to people in any industry because it gives them a better opportunity to control or direct their processes, and, perhaps more significantly, to permit prediction when process development work is conducted. I think that this paper will serve as a foundation paper for any work done in tanneries on poly-retan leather.

I have one question. Your data suggest that, although the initiation system is not interfered with by the chrome, the leather chrome content does not reflect itself very much in the absorption of the persulfate. Furthermore, the persulfate absorption determined by the difference between the amount given and the equilibrium concentration in the aqueous phases is a relatively constant value. This could suggest that some definite complex is formed with the collagen *per se.* I know from the previous paper that identification of the actual site of attachment can not yet be made. Can you give any indication at this time?

MR. E. H. HARRIS: At this time, the answer is no.

DR. PETER R. BUECHLER (PPG Industries, Inc.): In the so-called "gel coats" for fiber-glass/monomer combinations which are frequently used to form skis or other such items, it has been found that one can accelerate the process by using, besides the initiator, and even the initiator plus reducer, small amounts of such metals as cobalt and vanadium. There may have been an indication early in your paper that with more chromium there was a little better fixation. Also, I was impressed with the fact that you used such a low molar ratio of bisulfite to initiator in the latter part of your paper. I wonder if there might not be with the chrome some cobalt or vanadium to serve as an accelerator of the reaction? Or, perhaps Cr^{+3} might accelerate the reaction?

MR. HARRIS: I have made no determinations of trace elements so I can not comment. I would comment that the grafting reaction is the essential reaction, not just polymer formation within the skin. However, I really can't comment on the significance of your suggestions.

DR. BUECHLER: Did I understand the two parts of your paper correctly?

MR. HARRIS: In the beginning I related the persulfate ion absorption as it might possibly be related to the presence or absence of chrome. In the latter part of the paper, I examined the molar ratios of the reductants to the oxidant; we found the best efficiency at about 0.2.

DR. BUECHLER: Could there be a reductant in the chrome in the leather which helps to initiate the reaction, thus requiring less initiator?

MR. HARRIS: This could be a possibility. However some reductant will be required at room temperature where these experiments were conducted, since potassium persulfate or ammonium sulfate will not initiate polymerization at these temperatures.

DR. J. W. HARLAN (Eastern Regional Research Center): Ed, when you considered chrome level, did you have any work at zero chrome level?

MR. HARRIS: In the study reported here, the lowest chrome level was 1.8.

DR. PRENTISS: I have made some calculations on the data. Although there is some scatter in the percent polymer bound, statistically there is not a great difference in the percent polymer bound from the low to the high levels of chrome. Again this indicates that the chrome does not play a major part in the grafting processes.

Does the lower than the theoretical level of bisulfite used to produce the free radicals relate to the methods of use with regard to simultaneous addition of the two materials in the initiation step?

MR. HARRIS: I would like to investigate this, but do not have data at this time.

DR. PRENTISS: Thank you for a very excellent paper.